AFRL Projects to Replace Cadmium

JCAT Meeting

10-13 March, 2005

Greensboro, NC

Maj Timothy Allmann

Pollution Prevention R&D Team/MLSC
Air Force Research Laboratory

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OMB No. 0704-0188</td></tr>
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<tr><td colspan="2">1. REPORT DATE
MAR 2005</td><td>2. REPORT TYPE</td><td colspan="2">3. DATES COVERED
00-00-2005 to 00-00-2005</td></tr>
<tr><td colspan="3" rowspan="3">4. TITLE AND SUBTITLE
AFRL Projects to Replace Cadmium</td><td colspan="2">5a. CONTRACT NUMBER</td></tr>
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<tr><td colspan="2">5c. PROGRAM ELEMENT NUMBER</td></tr>
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<tr><td colspan="3">7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory,AFRL/MLSC,Wright Patterson AFB,OH,45433</td><td colspan="2">8. PERFORMING ORGANIZATION REPORT NUMBER</td></tr>
<tr><td colspan="3" rowspan="2">9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</td><td colspan="2">10. SPONSOR/MONITOR’S ACRONYM(S)</td></tr>
<tr><td colspan="2">11. SPONSOR/MONITOR’S REPORT NUMBER(S)</td></tr>
<tr><td colspan="5">12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited</td></tr>
<tr><td colspan="5">13. SUPPLEMENTARY NOTES
25th Replacement of Hard Chrome and Cadmium Plating Program Review Meeting, March 15-17, 2005, Greensboro, NC. Sponsored by SERDP/ESTCP.</td></tr>
<tr><td colspan="5">14. ABSTRACT</td></tr>
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Same as Report (SAR)</td><td rowspan="2">18. NUMBER OF PAGES
43</td></tr>
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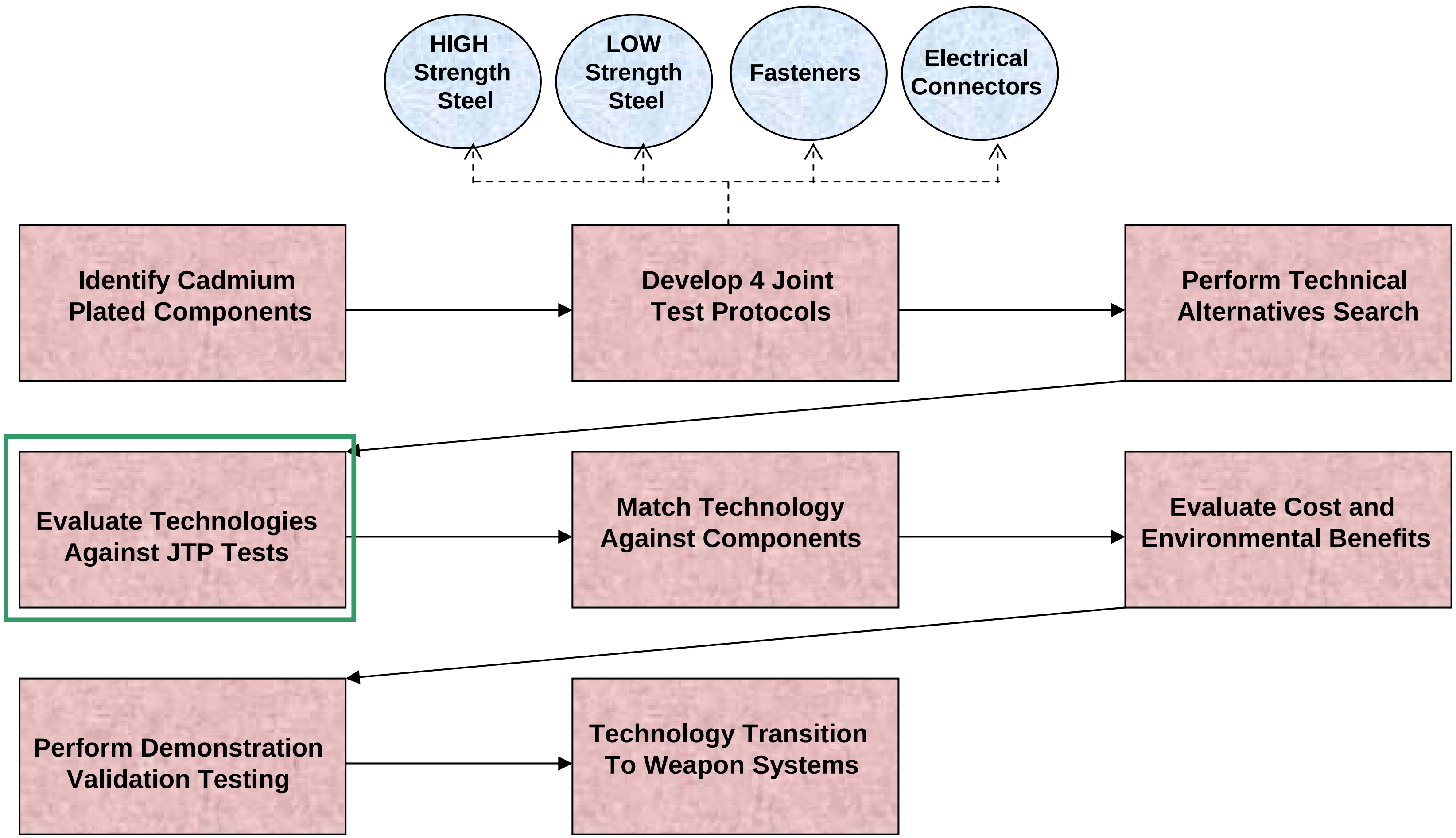
19a. NAME OF RESPONSIBLE PERSON

AFRL Projects to Replace Cadmium

- **Active Projects**
  - **Cd Alternatives: HSS Components JTP/Testing**
    - AFRL POC: Tom Naguy/Major Tim Allmann
    - Contractor: Concurrent Technologies Corporation
    - Stakeholders: AFRL, OO-ALC. AAMCOM, NAVAIR, ESTCP, Various OEMs
  - **APCVD Aluminum to Replace Cd**
    - AFRL POC: Tom Naguy/Major Tim Allmann/Dr. Eric Brooman
    - Contractor: New Jersey Institute of Technology
    - Stakeholders: AFRL, ARL, NAVAIR
  - **Magnetron Sputtering to Replace Cd (and Cr)**
    - AFRL POC: Tom Naguy/Dr. Eric Brooman
    - Contractor: Concurrent Technologies Corporation
    - Stakeholders: AFRL, ASC, OO-ALC

Cd Alternatives: HSS Components JTP

- **Program flow diagram and 4 Joint Test Plans**

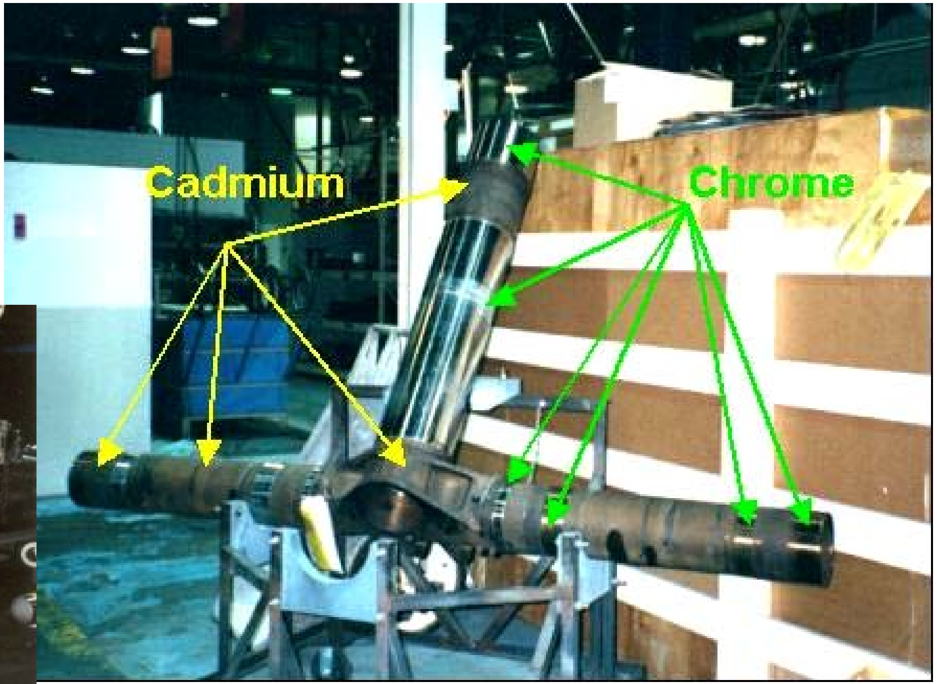


Cd Alternatives: HSS Components JTP

- **Project objective**
  - **Develop a test protocol for evaluating low-hydrogen-embrittlement cadmium plating alternatives for high-strength steel**
    - Support for test protocol from all Department of Defense service branches
      - Allow a coordinated approach for all high-strength steel applications
      - Facilitate and expedite implementation

Cd Alternatives: HSS Components JTP

- **Initial test protocol framework built on performance requirements for landing gear coatings**
  - **FED-STD-QQ-P-416** (Cd plating)
  - **MIL-STD-870B** (LHE-Cd)



Cd Alternatives: HSS Components JTP

- **Testing Phases**
  - **Phase I**
    - Hydrogen Embrittlement/Re-embrittlement
  - **Phase II**
    - General Properties
    - Adhesion
    - Corrosion
    - Lubricity
    - Repairability
  - **Phase III**
    - Fatigue
- **Status**
  - **Phase I in progress (NAVAIR), ECD: early Apr**
  - **Phase II/III in contracting for April start**

APCVD Al as Replacement for Cd

- **Project Objective**
  - **Investigate the use of atmospheric chemical vapor deposition (APCVD) to produce Al coatings of high quality on high strength steel components**
    - Permit high production throughput
    - Provide good throwing power/coverage
    - Meet environmental goals
    - Be cost effective
    - Lead to a suitable implementation plan
  - **Three year SERDP project duration**
    - **SERDP 04 (late start) - Project PP1405**
      Atmospheric Pressure Chemical Vapor Deposition of Al

APCVD Al as Replacement for Cd

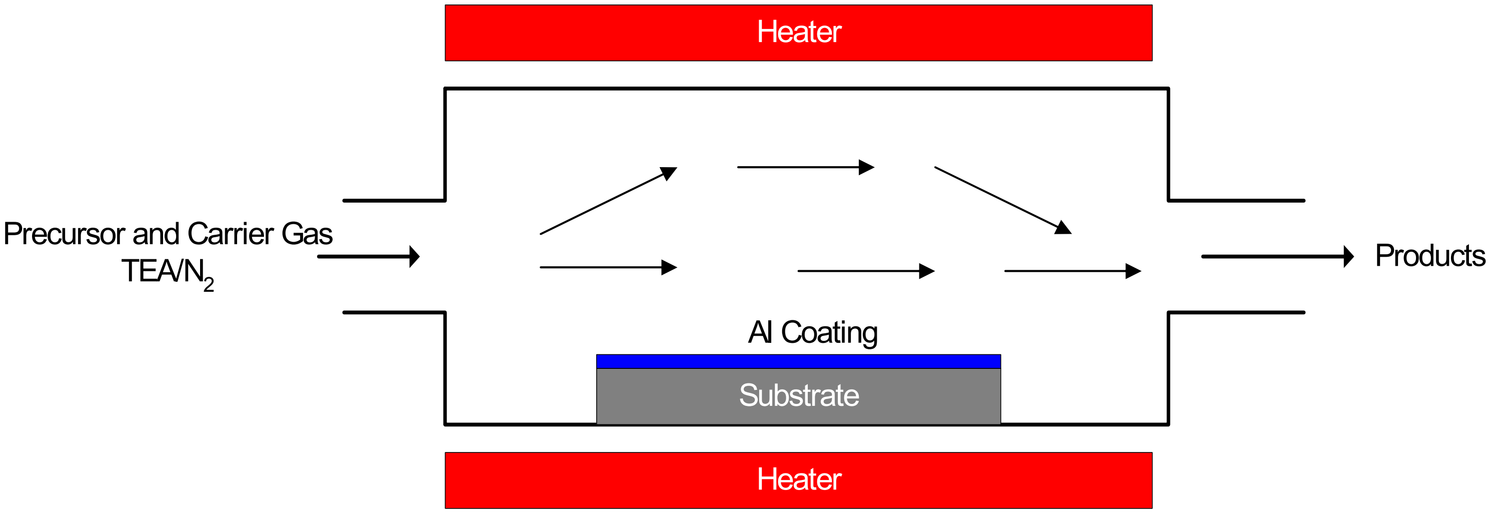
- **Project Team**
  - **Air Force Research Laboratory** (*Requirements, Project Management*)
    - Major Tim Allmann/Dr. Eric Brooman
  - **Naval Air Systems Command** (*Requirements, Testing*)
    - Kate Horspool (NAVAIR, PAX River)
  - **Army Research Laboratory** (*Requirements, Testing*)
    - Dr. John Beatty/Brian Placzankis
  - **New Jersey Institute of Technology** (*Process Development*)
    - Prof. Roland Levy (Principal Investigator)
  - **Boeing Company** (*Industry Liaison, Technology Insertion*)
    - Steven Gaydos

APCVD Al as Replacement for Cd

- **Technology Background**
  - **Al has advantages over Cd as coating material**
    - Not a hazardous chemical (OK under MIL-DTL-83488)
    - Good corrosion resistance, resistant to aircraft fluids
    - Withstands higher operating temperatures
    - Lower vapor pressure than Cd
  - **APCVD technology has advantages**
    - CVD processes are well established for a wide range of coatings (equipment, supplies available commercially)
    - High vacuum chambers, etc. not required
    - Simple NLOS process (e.g., surface catalyzed reaction)
    - Al deposits formed at relatively low temperatures (<400^{o}F)
    - Hydrogen embrittlement avoided

APCVD Al as Replacement for Cd

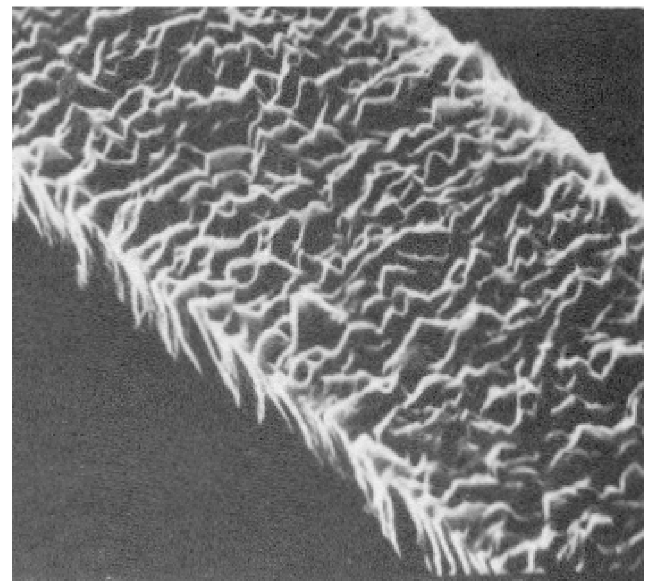
- **Reactor Schematic**



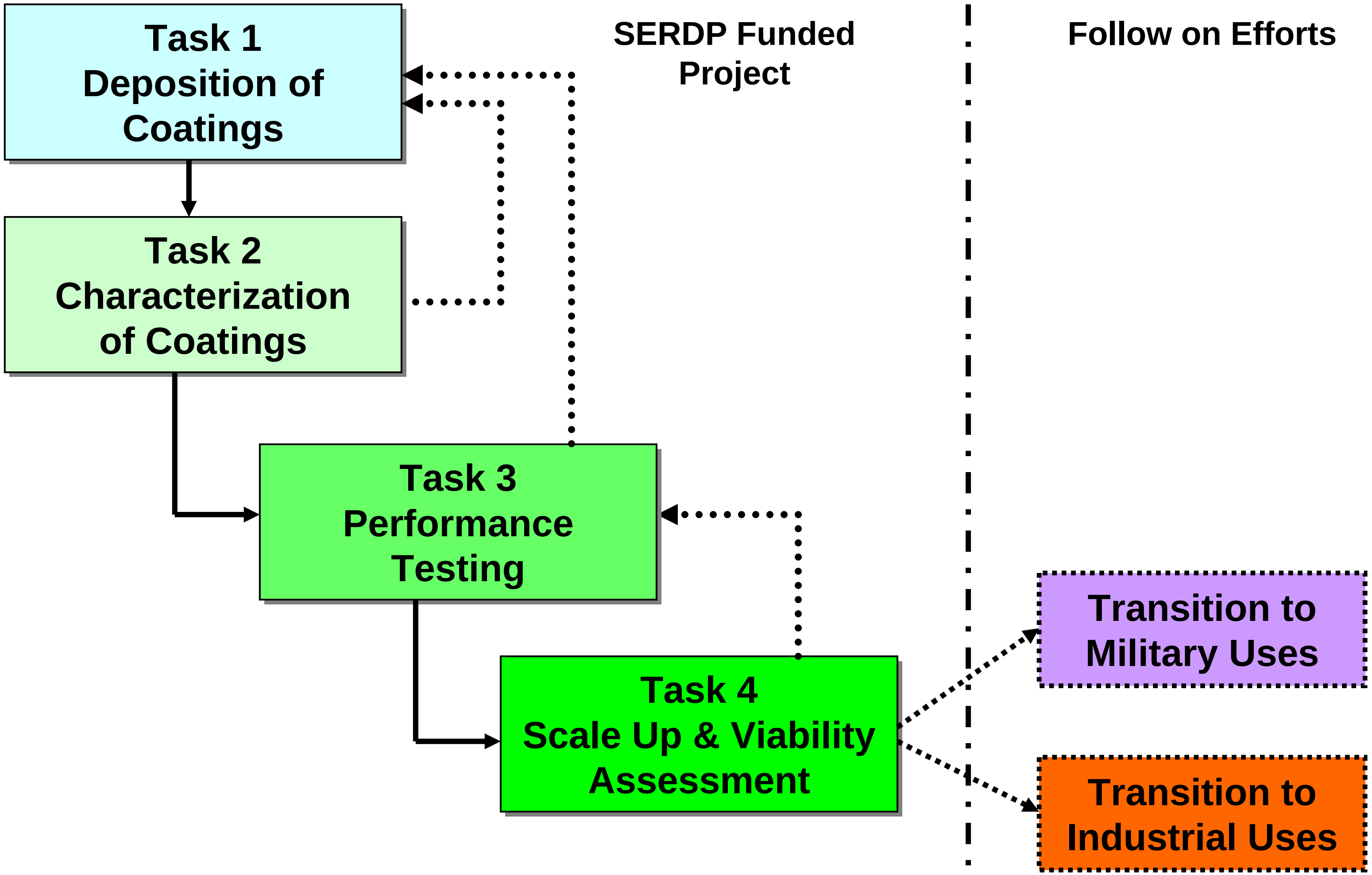
APCVD Al as Replacement for Cd

- **Example of Conformal Coverage of Al on Si**

~ 0.002 inch



APCVD Al as Replacement for Cd



APCVD Al as Replacement for Cd

- **Task 1: Deposition of Al Coatings**
  - **Set up and calibrate bench-scale equipment**
  - **Deposit Al coatings on HSS substrates**
  - **Measure growth rate and identify rate limiting parameters**
  - **Determine nature of growth mechanism**
  - **Optimize growth conditions from experimental data**
- **Progress to Date**
  - **Contract start date was August 2004**
  - **Task 1 Accomplishments**
    - Post Doc student with experience in CVD assigned to project
    - Bench-scale reactor was set up and checked out; N_2 reactor flushing equipment installed
    - Suppliers of the triethylaluminum precursor have been identified
    - Experiments on calibrating the temperature profiles and gas flows in the reactor were performed

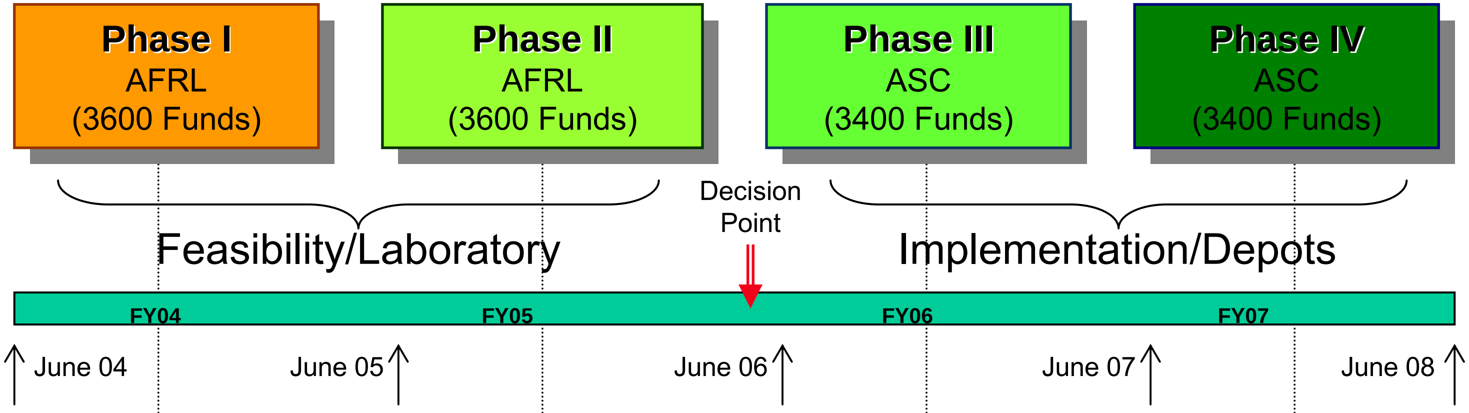
APCVD Al as Replacement for Cd

- **Work Planned This Quarter**
  - **Connect the precursor tank to CVD reactor**
  - **Conduct flow rate calibration for precursor (triethylaluminum)**
  - **Deposit aluminum on steel coupons**
  - **Begin preliminary coating characterization**

Magnetron Sputtering to Replace Cd

- **Project Objective**
  - **Investigate feasibility of using PVD/magnetron sputtering to deposit improved aluminum and hard coatings as replacements for Cd and electroplated hard Cr (EHC)**
    - Primarily replace IVD Al + chromated post-treatments
    - Also evaluate if hard coatings could replace EHC
    - Coat inside **and** outside diameters/surfaces
    - Provide good throwing power/coverage
    - Allow high production throughput
    - Meet environmental goals
    - Be cost effective over life cycle
  - **Four Phase/three year Project**

Magnetron Sputtering to Replace Cd



Technology Assessment & Screening Tests
- Requirements Analysis
- Technology Assessment
- Screening Test Plan
- Coating Deposition
- Screening Testing
- Test Report
- Recommendations
- Report & Briefing

Coating Characterization & Insertion Plan
- Characterization Test Plan
- Coating Deposition
- Characterization Test Plan
- Test Report
- Cost Benefit Analysis
- Recommendations
- Prototype Equipment Design
- Preliminary Technology Insertion Plan
- Report & Briefing

Coating Optimization & Prototype Design
- Optimization Test Plan
- Coating Deposition & Optimization
- Test Report
- Final Cost Benefit Analysis
- Design of Prototype Unit
- Recommendations
- Report & Briefing

Prototype Installation & Demonstration
- Critical Design Review
- Installation Plan
- Demonstration Plan
- Prototype Fabrication
- Equipment Installation & Check Out
- Demonstration Testing
- Test report
- Final Report & Briefing

Magnetron Sputtering to Replace Cd

- **Progress to Date**
  - **Contract start date was June 2004**
  - **Task 1 Accomplishments**
    - **Technical and Management Work Plan**
      - Submitted by Contractor and approved by AFRL
    - **Requirements Analysis and Technology Assessment Report**
      - Submitted by Contractor and approved by AFRL
      - Coatings being considered as Cd alternatives

        Al (dense, pore free) **Al-Mn** (≤ 44%)

        Al-Mo (≤ 40%) **Al-W** (≤ 20%)
    - **Screening Test Plan**
      - Submitted by Contractor and approved by AFRL
      - Testing, sample, and coating parameters defined
    - **Request for Quotation**
      - For coated samples from suppliers for screening tests
      - Submitted by Contractor and approved by AFRL
      - Sent to suppliers in February, 2005

Magnetron Sputtering to Replace Cd

- Work Planned by Contractor
  - Send approved RFQ for coatings to qualified vendors/suppliers
  - Obtain aluminum coated samples
    - Other Cd alternatives may be approved later
    - Baselines and benchmarks will be established
  - Perform Screening Tests and analyze data
  - Prepare draft Phase I Final Report for Air Force review
  - Decision Point to proceed with Phase II

Magnetron Sputtering to Replace Cd

- **Points of Contact**
  - Dr. Eric Brooman, Air Force Research Laboratory, (937) 656-6063, Eric.Brooman@wpafb.af.mil
  - Chuck Valley, Aeronautical Systems Center, (937) 255-3567, Charles.Valley@wpafb.af.mil

Back-up Slides

Cd Alternatives: HSS Components JTP

- Project Team/Stakeholders

DoD

- Air Force Research Laboratory
- Ogden Air Logistics Center, Hill AFB
- Air Force Materiel Command
- Naval Aviation Center
- Army Aviation and Missile Command
- Environmental Security Technology Certification Program
- Joint Cadmium Alternatives Team

Manufacturers

- Boeing
- Goodrich
- Lockheed-Martin
- Messier-Dowty

Contract Research

- Concurrent Technologies Corporation/NDCEE

Cd Alternatives: HSS Components JTP

- Problem statement
  - Cadmium containing solutions from plating, rinse waters, wash-down are hazardous materials
  - Primary cadmium alternative dimensionally limited
    - Ion vapor deposited aluminum cannot coat deep recesses and blind holes
    - Recesses/holes common to aircraft landing gear parts
  - Alternative to low-hydrogen-embrittlement cadmium (LHE-Cd) plating needed that can be used on all high-strength steel applications

Cd Alternatives: HSS Components JTP

- A Test Protocol identifies
  - Engineering performance requirements
  - Test methods to demonstrate performance characteristic
  - Criteria for acceptable performance
- A Test Protocol does not
  - Identify/select a material or process
  - Impose processing restrictions on candidates
  - Implement a material or process into production
  - Define process control limits

Cd Alternatives: HSS Components JTP

- **Input from Team Members**
  - **Discuss performance requirements**
    - All information needed to make implementation decisions
    - End item and process
  - **Discuss tests to verify/validate performance**
    - Test methods
    - Pass/fail criteria
  - **Define issues and concerns**

Cd Alternatives: HSS Components JTP

- **Each test requirement includes**
  - **Test descriptions**
  - **Test rationales**
  - **Test methodologies**
  - **Equipment/instrumentation details**
  - **Data analysis methods** (where data manipulation is necessary)

Cd Alternatives: HSS Components JTP

- **General Properties**
  - **Appearance**
    - Smooth, continuous without defects
  - **Throwing power and alloy composition uniformity**
    - Need to know that alloy is within proper limits
    - Use XRF to measure composition and thickness
  - **Strippability**
    - Remove coating within 60 minutes
    - Replate coating and pass adhesion and corrosion tests
  - **Galvanic Potential (Corrosion)**
    - Electrochemical Analysis

Cd Alternatives: HSS Components JTP

- **Adhesion Testing**
  - **Adhesion to substrate**
    - Bend to break
    - No observed separation from basis metal at 4x magnification
  - **Paint adhesion to coating**
    - Waterborne (MIL-PRF-85582) primers
    - Dry, 24 hr and 7 day de-ionized water exposure
    - Scribe with tape pull

Cd Alternatives: HSS Components JTP

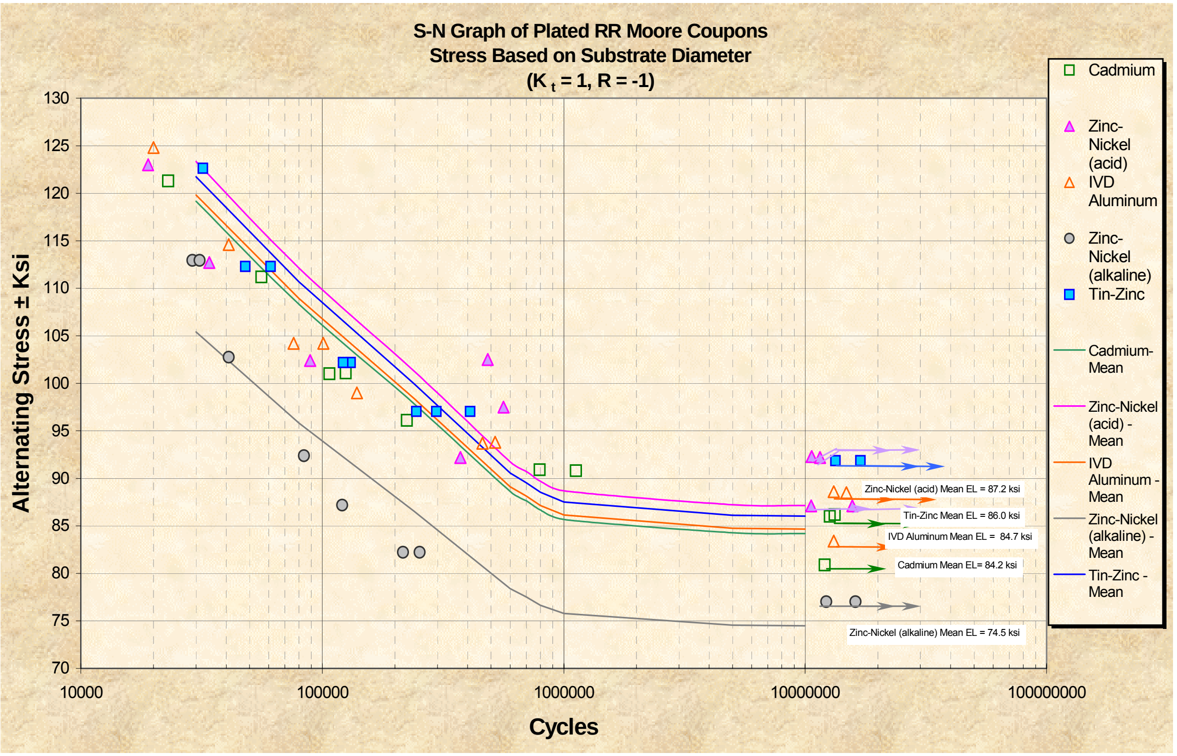
- **Lubricity Testing**
  - **Run-on, break-away torque**
    - 3/8” and 5/8” bolts
    - Non-locking nut
    - Lubricated with anti-seize compound
    - No environmental exposure
  - **Torque-tension**
    - 3/8” and 5/8” bolts
    - Locking nut
    - Lubricated with anti-seize compound

Cd Alternatives: HSS Components JTP

- Repairability
  - Bend adhesion
  - Paint adhesion
  - Corrosion resistance (B 117 salt fog, scribed, un-scribed)
  - Hydrogen embrittlement

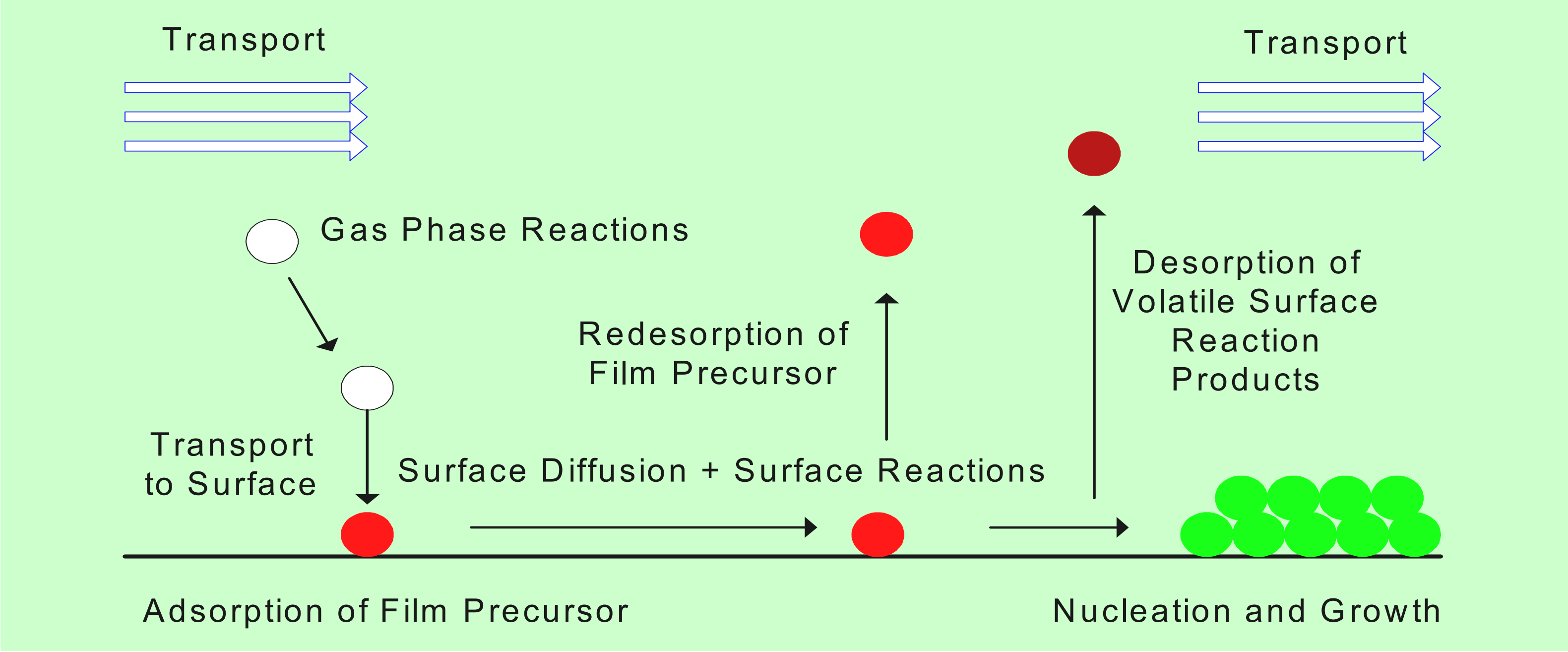
Cd Alternatives: HSS Components JTP

- **Fatigue Testing**
  - **Rotating Beam** (RR Moore)
    - Per ASTM E468, ISO 1143
    - SAE 300 M coupons, smooth (K_t=1.0) and notched (K_t=2.6)



APCVD Al as Replacement for Cd

- Process Schematic



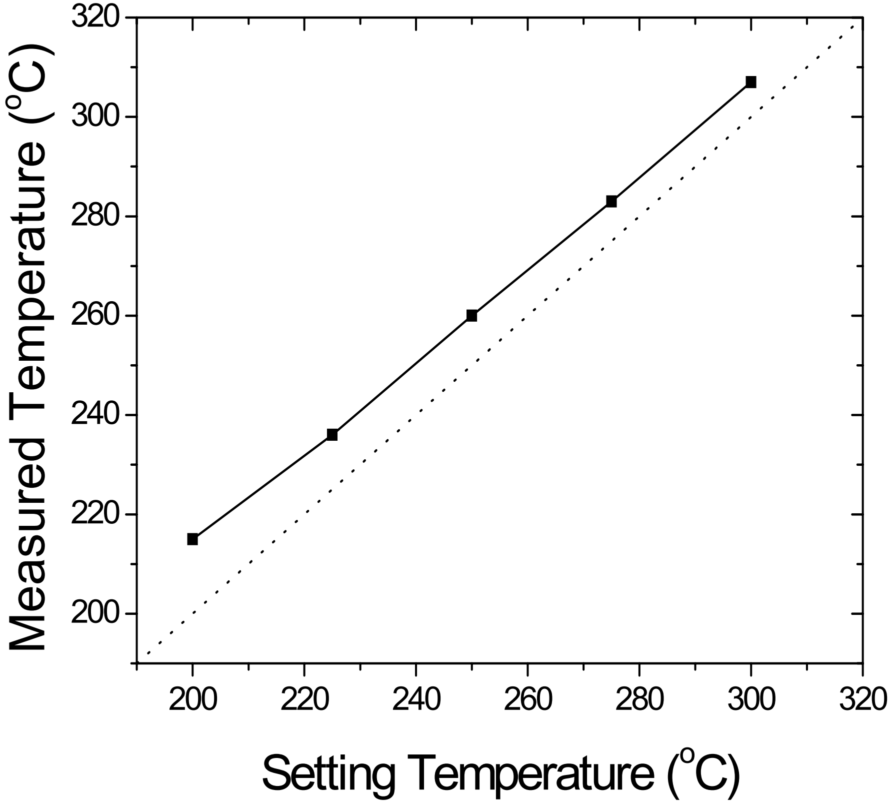
APCVD Al as Replacement for Cd

- **Experimental Reactor – Set Up for Temperature Measurements**

- **Place type K thermocouple inside chamber where the sample is to be located**
- **Vary temperature over experimental range of 200°C to 300°C**
- **Compare furnace setting to thermocouple reading**

APCVD Al as Replacement for Cd

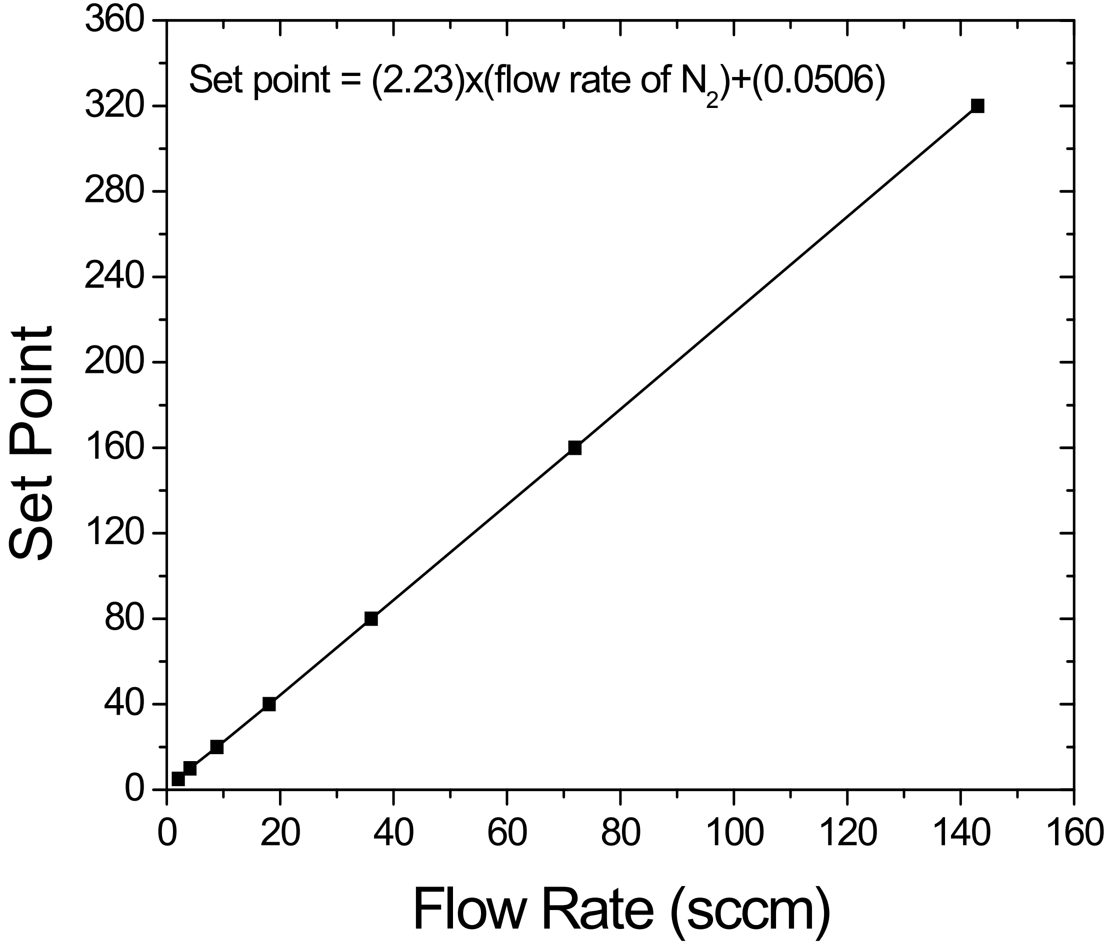
- **Temperature Calibration**



- **Measured temperature is higher than set point**
- **Temperature difference is reduced as setting temperature increases**
- **Difference is about 14°C for the range from 200°C to 225°C**

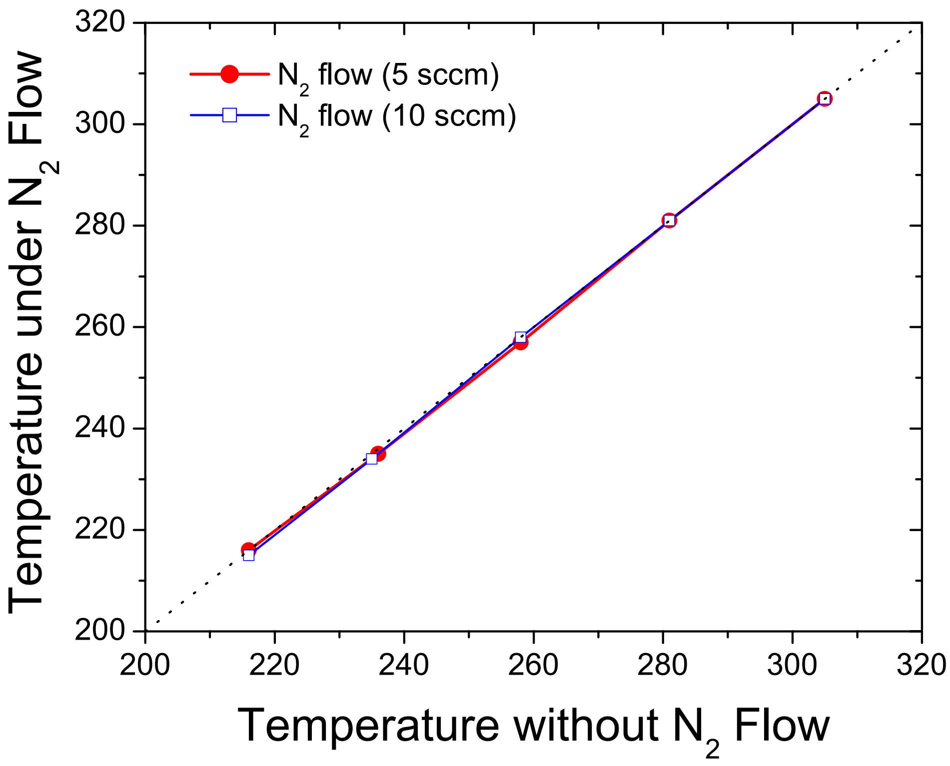
APCVD Al as Replacement for Cd

- **Flow Rate Calibration**



APCVD Al as Replacement for Cd

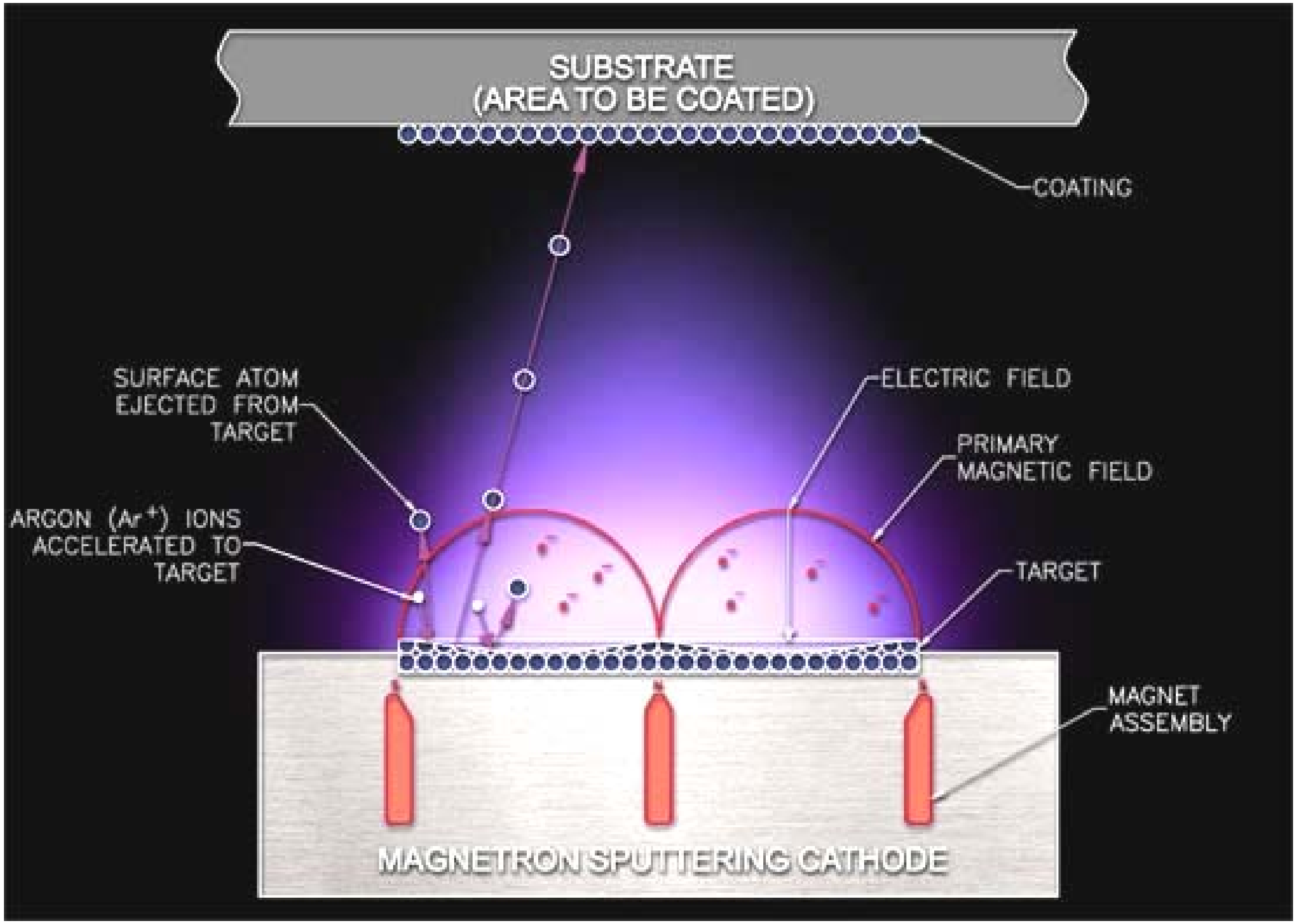
- Temperature Change Under N2 Flow



- Place type K thermocouple inside chamber as same as temperature calibration
- N2 flow rate: 5 sccm and 10 sccm
- Compare the temperature change under N2 flow to that without N2 flow
- No significant change of temperature due to N_2 flow is observed

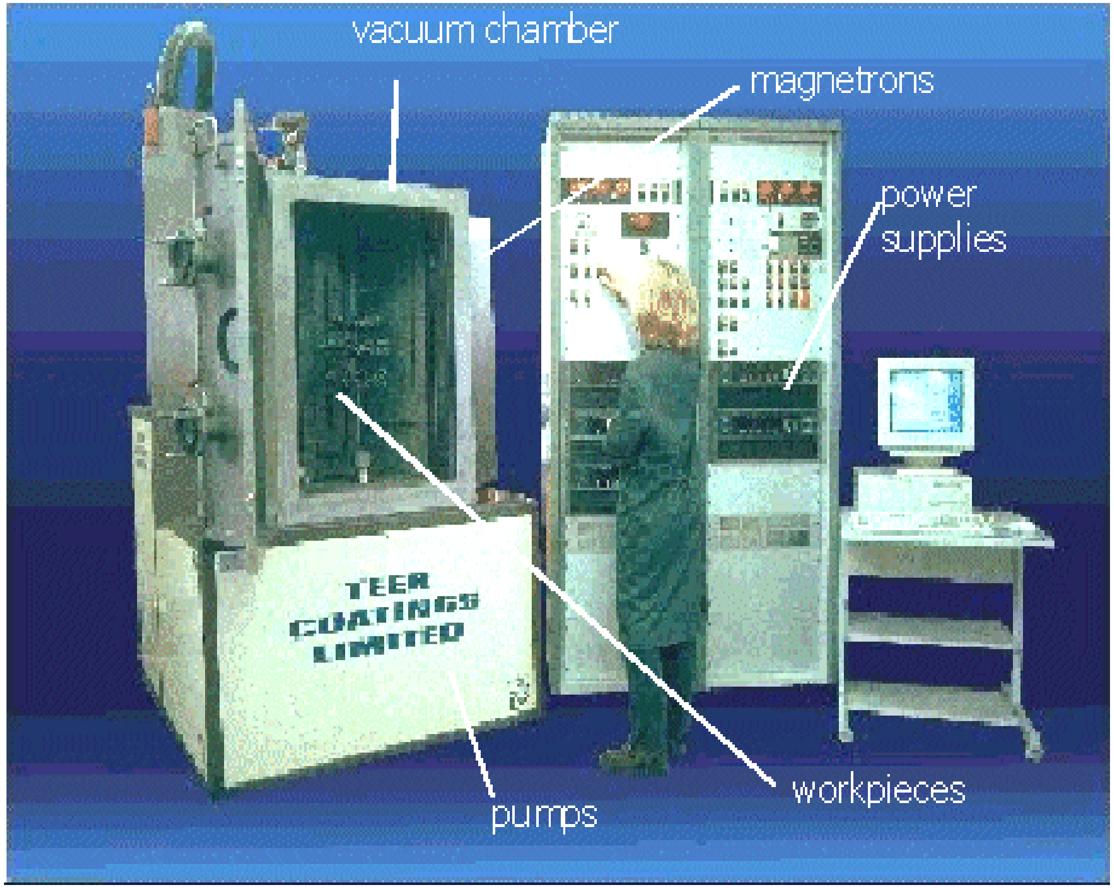
Magnetron Sputtering to Replace Cd

- **Process Schematic (planar magnetron)**



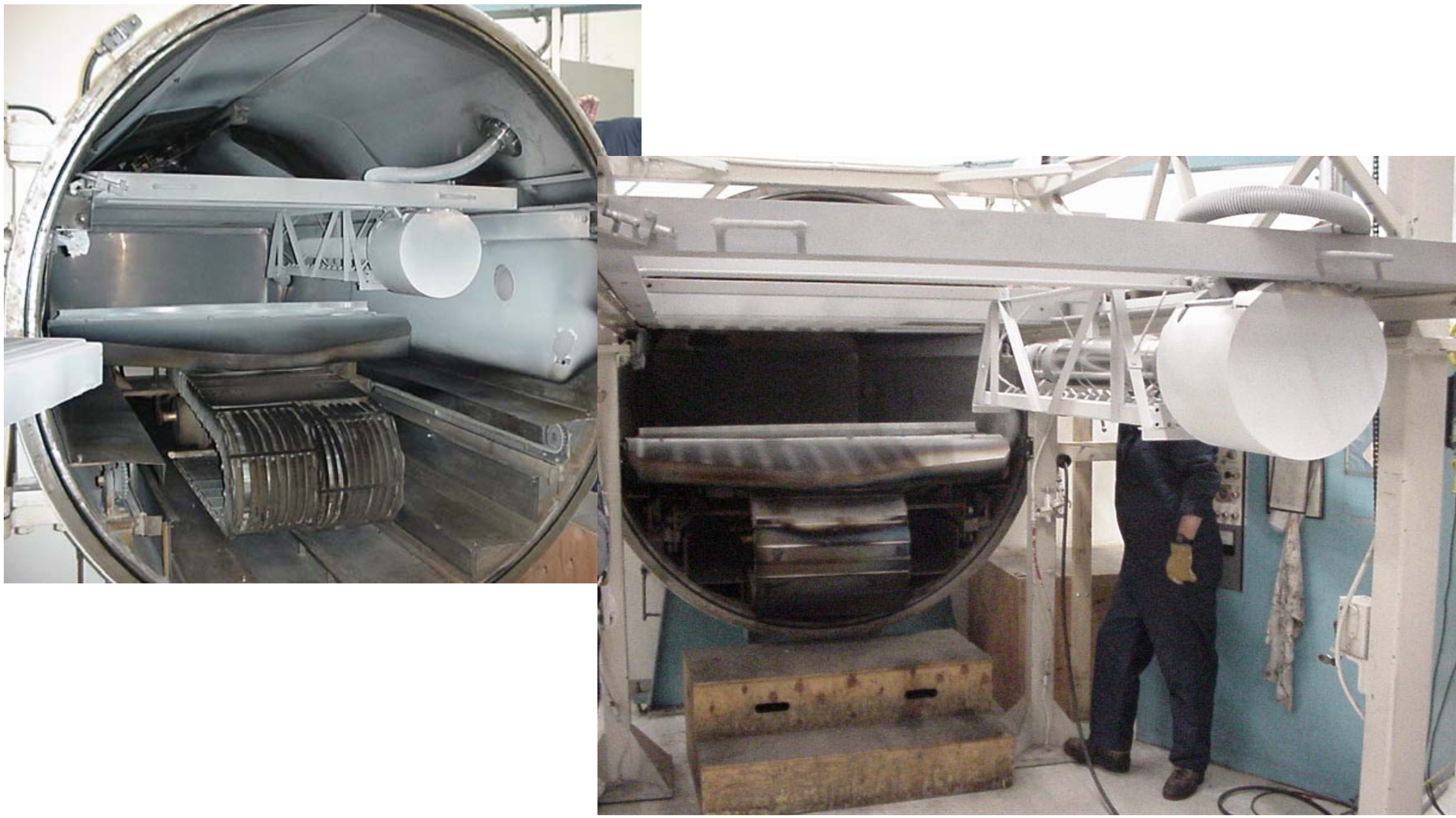
Magnetron Sputtering to Replace Cd

- **Example of Small commercial MSC System**



Magnetron Sputtering to Replace Cd

- “Plug & Coat” Rack Installed in IVD System **for LG**



Magnetron Sputtering to Replace Cd

- **Task 1: Requirements Analysis & Technology Assessment**
  - **Requirements Analysis**
    - Parts currently coated with Cd
    - Parts that could be coated with Cd alternative(s) (i.e. MS Al)
    - Parts currently coated with Cr
    - Parts that could be coated with Cr alternative(s) (i.e., MS hard coatings)
  - **Technology Assessment**
    - MS coatings – current status of potential Cd and Cr alternatives
    - MS equipment – commercially available or near commercial
    - MS materials and supplies – commercially available
  - **Requirements Analysis & Technology Assessment Report**
  - **Screening Test Plan**

Magnetron Sputtering to Replace Cd

- **Vendor/developer draft Qualification Questionnaire**

Contact Information

Process Name

Company Name: Address: City: State: Zip Code: Telephone Number: Email Address: Web Site Address: Technical Point of Contact: Title: Telephone Number: Email Address

Technology Requirements

- High rate deposition capability
- Ability to deposit to coating thicknesses in the range of 1 -10 mils (1 mil for Al and up to 10 mils with hard coatings)
- Ability to coat ID and OD in single pump down is a plus
- Maximum part size is 500 lbs at 6' x 13"; bore lengths can be 6' long and diameters from a few inches to 13"
- Ability to coat multiple small components (say 6" x 1 to 2" in diameter)
- Materials to be coated include high strength steel (300M, 4340, 4130), 7000 series Al, and stainless steel
- Coatings - aluminum, aluminum-manganese, 4340, 7000 series Al, hard coatings (e.g., nitrides, oxides, alloys, etc.)

Please Complete the Following to the Fullest Extent Possible

- Please describe your technology/process:
- What is the maximum size part that can be treated using your technology?
- Number of small components (e.g., 2-3" x 4-12"), medium components (3-4" x 13-24"), and large components (4-8" x 24-60") that can be treated in a single batch and whether those components can be coated both on the internal surfaces (such as IDs) as well as the external surfaces, simultaneously
- Issues associated with neutralization of energetic particles
- Issues associated with macro-particles
- Issues associated with rough surfaces (what's the maximum rms roughness that can be tolerated without concerns with shadowing)
- Specialty maskants required (e.g., tantalum foil, stainless steel foil)

(continued)

- Special cathode geometries (sputtering or cathodic arc) or crucibles (electron beam - especially when evaporating aluminum) needed
- The rates of deposition that are possible and those used to obtain a coating with acceptable film morphology
- The substrates that can be treated (without observing degradation of properties, such as in high strength steels)
- Film morphologies that can be obtained without the use of high temperatures or high levels of bombardment/biasing that would also produce high local temperatures
- Other than aluminum, the hard coatings that can be deposited using the process
- The stage of development of the process (e.g., research, development, or commercially available); maximum coating thickness that can be obtained without high internal residual stresses being produced such that delamination under load or under environmental conditions is imminent (again, without the use of high temperatures) - if layering is needed, please state so
- Systems sold and/or commercial and/or military applications (references preferred)
- ROM cost for the production equipment or a cost per unit area per thickness coated
- Any environmental or occupational safety concerns or required personal protective equipment
- The need for ancillary equipment (air gantry, planetary gears, water cooling - chiller, clean room, etc.)
- Evacuation time (pump down cycle)
- Process controllability (degree to which the system must be monitored during deposition)
- Coatings with which you have experience in the system that you suggest be investigated
- Are technical data sheets or other forms of product information available?

Magnetron Sputtering to Replace Cd

- Task 2: Coating Deposition and Screening
  - Selection of qualified vendors and suppliers
  - Coating deposition on HSS samples by vendors
  - Testing and analysis of data
  - Screening Test Report
  - Down selection and recommendations

- Phase I Final Report and Briefing

Magnetron Sputtering to Replace Cd

- **Requirements Analysis & Technology Assessment**

MS Systems - Yes	MS Systems - Maybe	MS Systems - No
Marshall Laboratories, Inc.	Balzers	Bodycote K-Tech, Inc.
Teer Coatings, Ltd.	Chessen Group, Inc.	Cametoid, Ltd.
Ulvac Technologies, Inc.	Fraunhofer*	DVTI, Inc.
	Hauser Techno Coating	Ionic Fusion Corp.
	IonEdge Corp.	Izovac ltd.
	Vactec Coatings, Inc.	Mat-Vac
	Veeco	Paradigm Shift
	Vergason Technology, Inc.	Sulzer Metaplas
		Von Ardenne
Equipment/Supplies - Yes	**Equipment/Supplies - Maybe**	**Equipment/Supplies - No**
Advanced Energy	Angstrom Sciences, Inc.	Anatech, Ltd.
Gencoa	BOC Edwards	Isoflux, Inc.
	Denton Vacuum	Kurt J. Lesker Co.
	Leybold Vacuum	Telic Co.
	Varian, Inc.	
Developers - Yes	**Developers - Maybe**	**Developers - No**
Benét Laboratories	AJA	Cemecon, Inc.
	Army Research Laboratory	LLNL
	EMPA/IFP	Inst. Of High Current Electronics
	New Jersey Institute of Technology	Paradigm Shift Technologies, Inc.
	Southwest Research institute	Sub-One Technologies

Magnetron Sputtering to Replace Cd

- **Vendors/Developers by PVD Equipment Type**

Planar	Cylindrical/Inverted	Pulsed
Fraunhofer?	Benét Laboratories	Chessen Group, Inc.
Hauser Techno Coating	Cametoid, Ltd.	Fraunhofer
IonEdge Corp.	EMPA/IFP	Teer Coatings
Ionic Fusion?	Marshall Laboratories, Inc.	
Chessen Group, Inc.	Paradigm Shift Technologies, Inc.	
Izovac ltd.		
Southwest Research institute		
Sulzer Metaplas		
Teer Coatings		
Ulvac		
Vactec Coatings, Inc.		